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Photocatalytic Reaction Pathway and Mechanism of Degradation Of Pesticide Using Nano Catalysts

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Abstract

In the present study, dichlorvos was degraded with photocatalytic active p-type semiconductor and n - type semiconductors. The nano - WO_3 was synthesized fromsodium tungstate andnano - TiO_2 was synthesized through sol-gel technique from titanium (IV) isopropoxide by hydrothermal treatment. The synthesized materials were characterized by different techniques such as XRD, FTIR, and SEM . In order to find out their photocatalytic ability and degradation of dichlorvos, experiment was carried out in aqueous suspension under UV light. The reaction pathway and mechanism were studied. From the evaluation, nano- TiO_2 showed higher activity when compare with other catalyst.

Keywords: *Dichlorvo; Degradation; Photocatalyst; Nano - TiO_2.*

1. INTRODUCTION

The environment and the whole lot connected with it's been a major difficulty of the general public, due to the fact maximum of our ecological structures particularly water are being continuously contaminated by home and commercial pollution. At some stage in the past numerous many years, the boom of population and the hobby in industry and agriculture have drastically altered the environment and reduced the natural sources. The continual and toxic organic substrates present in waste water effluent have to be removed or destroyed before discharge to the environment. Already existing methods like adsorption or biological treatment appear to have many drawbacks for the reason that former entails only section transfer of the pollution without degradation and the latter cannot be implemented to contaminants which can be toxic to the micro-organism (Hoffmann *et al.*. 1995). Semiconductor assisted photocatalysis is a promising environmentally benign technique which has been broadly and efficaciously used for the elimination of pollution (Ragnarsdottir, 2000).

The organophosphorous insecticides are comprised within the ten most broadly used insecticides all around the global. They're extremely poisonous appearing on acetylcholinesterase hobby (Mileson *et al.*. 1998; Mennear and Dichlorvos, 1998). Dichlorvos (2,2-dichlorovinyl-o,odimethyl phosphate) become commercially synthetic in 1961 and it is used for insect manage in meals storage areas, greenhouses and barns. It's also used for controlling parasites and bugs in homes, aircraft and outside regions (as aerosols, liquid sprays).

On this take a look at, the photocatalytic degradation of dichlorvos using Graphite oxide (GO), Commercial TiO_2 (C-TiO_2), WO_3,nanoTiO_2 as catalysts has been investigated. the objectives have been: (i) to assess the kinetics of pesticide disappearance (ii) to evaluate the photocatalytic efficiency of the catalysts.The photocatalytic degradation of dichlorvos, the use of TiO_2 has already been studied with the aid of other researchers. Harada *et al.*. (1990), tested the charge of the photocatalytic oxidation of dichlorvos the use of rutile TiO_2 and TiO_2/pt as catalysts. Naman *et al.*. (2002), Lu *et al.*. (1996) and Balkaya (1999) examined the effect of various parameters just like the initial awareness of dichlorvos, the addition of salts, the addition of various sensitizers, and many others. No significant attempt has been made, from previous researchers, which will take a look at the photocatalytic efficiency of nano- TiO_2 on dichlorvos oxidation and the elements affecting it.

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2. EXPERIMENTAL METHODS

2.1 Reagents and Materials

Dichlorvos analytical grade (92% purity) was purchased from UPL Ltd (Gujarat) and was used without any further purification.. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area 56 m^2 g_1) was purchased from LobaChemie Pvt Ltd. Sodium Nitrate and Potassium Permanganate was purchased from Emplura. Titanium (IV) Isopropoxide was obtained from Sigma - Aldrich. Doubly distilled water was used throughout the work.

2.2 Material Synthesis

The detailed synthesis procedure for pure GO is given in our previous published report (Yeh *et al.*. 2010).

2.2.1 Preparation of WO_3:

The detailed synthesis procedure for pure WO_3 is as per the reported literature (Nogueira, 2004).

2.2.2 Preparation of TiO_2 nanoparticles

In the synthesis of TiO_2 particles, Titanium tetra isopropoxide was used as a precursor and was mixed with HCl, ethanol and deionized water mixture, stirred for half an hour, in pH range of 1.5. 10ml of deionized water was added to the above mixture and stirred for 2 hours at room temperature. Finally, the solution was dried at temperature and the powder was heated at 120 ºC for 1 hour.

2.2.3 Catalysts characterization

High-resolution transmission electron microscopy (HRTEM; JEOL 2100F, Japan) and scanning electron microscope (SEM; JEOL JSM-6700F, Japan) was used to explore the microstructure of the GO composites specimens. The crystal structure of the samples was characterized by powder X-ray diffraction (XRD) using a RIGAKU RINT-2000 (Japan) diffractometer with Cu Kα radiation, excited at 40 kV and 40mA. Fourier-transform infrared (FTIR) spectroscopy in diffused reflectance mode was conducted using a JASCO FTIR-4100 (Japan) spectrometer.

2.3. Irradiation procedure

Irradiation experiments were carried out in a 500 ml Pyrex UV reactor equipped with a diving Philips HPK 125 W high-pressure mercury lamp. The lamp was jacked with a water-cooled Pyrex filter restricting the transmission of wavelengths bellow 290 nm. The tap water cooling circuit was used to remove IR radiation preventing any heating of the suspension (30–350 C). Dichlorvos solution (10 mg L^{-1}, unless otherwise stated) with the appropriate amount of catalyst was magnetically stirred before and during the illumination. The suspension was left for 30 min in the dark, prior to illumination, in order to achieve the maximum adsorption of the pesticide onto semiconductors surface. The pH was not adjusted unless Otherwise stated. At specific time intervals samples were withdrawn from the reactor.

3. PHYSICO - CHEMICAL CHARACTERIZATIONS

The XRD pattern of commercial P-25 titania in which anatase and rutile phases are composed as 75:25. The presence of rutile phase is found at 2 theta value of 27.32 and the remaining peaks are corresponding to anatase. The high intensity peak shown at 25.33 is corresponding to 101 plane of anatasetitania. All of the reflection patterns of the WO_3 could be indexed to a monoclinic phase.

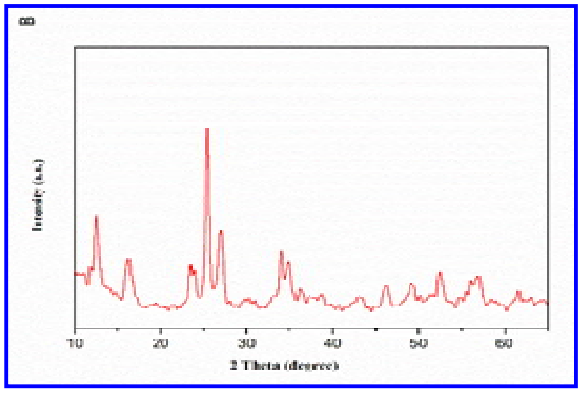

Fig. 1: X-Ray Diffraction pattern of TiO_2

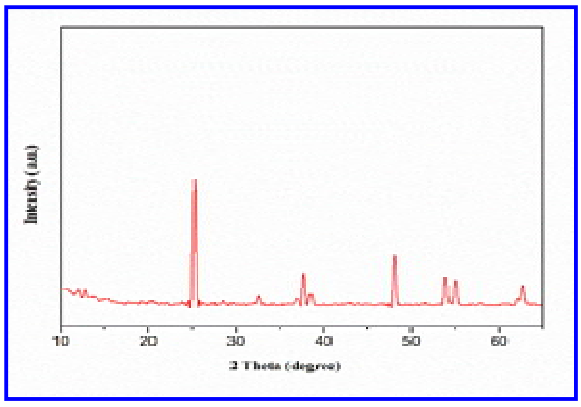

Fig. 2: X- Ray Diffraction patterns ofWO_3

The surface morphology of both the catalysts was viewed using scanning transmission electron microscopy and the results are shown in Fig. 3, 4, 5. As seen from the images, the surface was covered by large number of TiO_2 nanoparticles. In WO_3, though the particle shapes are poorly defined, three different morphological patterns were clearly observed.: irregular plates, nano wires, agglomerated particles.

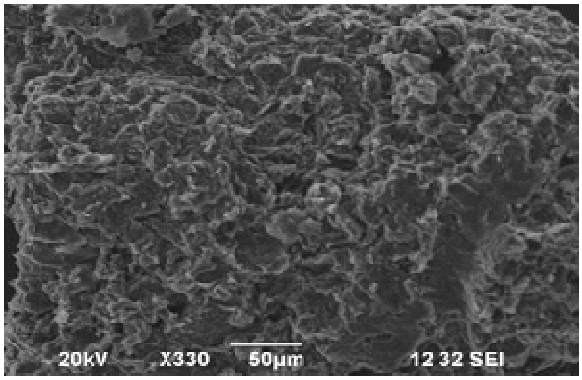

Fig. 3: Scanning Electron Microscopy image of GO

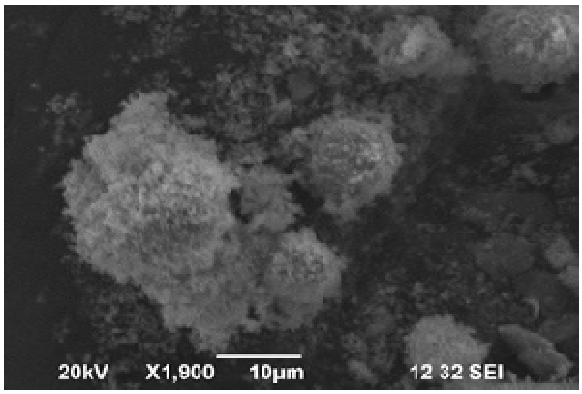

Fig. 4: Scanning Electron Microscopy image of TiO_2

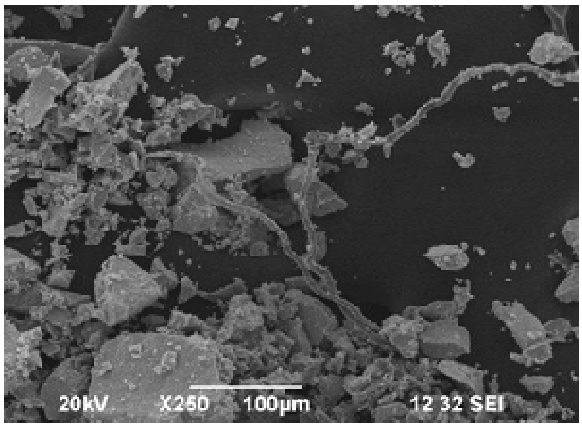

Fig. 5: Scanning Electron Microscopy image of WO_3

In all the FTIR spectra (Fig. 6), a peak is observed at 3200-3500 cm^{-1} corresponding to O-H stretching frequency (Paredes *et al.*. 2008) and this particular peak is broader in pure GO. The stretching frequency of C=O is found at 1690 cm^{-1} .The tertiary alcoholic group is detected at 1390 cm^{-1}. The peak for phenolic O-H is observed in GO at 1230 cm^{-1}.

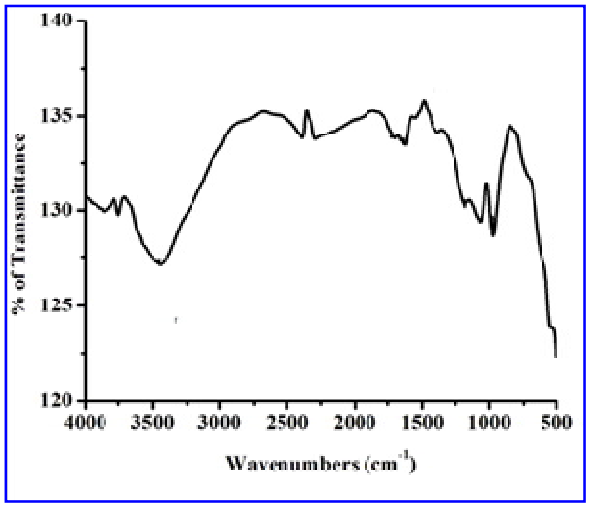

Fig. 6: FTIR spectra of pure GO

4. PHOTOCATALYTIC DEGRADATION PATHWAYS AND DEGRADATION

4.1. Primary degradation

The ability of the semiconductors to act as sensitizers and consequently to enhance the photodegradation of the organic pollutants is attributed to their electronic structure which is characterized by filled valence band and an empty conduction band. When the semiconductors are illuminated with energy greater than their bandgap energy (Eg), excited high-energy states of electron and hole pairs are produced:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$WO_3 + h\nu \rightarrow e^- + h^+ \quad (2)$$

These generated species can either recombine and dissipate the input energy as heat or react with electron donors or electron acceptors which are adsorbed on the semiconductor surface or trapped within the surrounding.

$$(O_2)_{ads.} + e^- \rightarrow (O_2^{\bullet -})_{ads.} \quad (3)$$

$$h^+ + H_2O \rightarrow H^+ + OH^- \quad (4)$$

$$OH^- + RH \rightarrow H_2O + R^{\bullet} \quad (5)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow CO_2 \quad (6)$$

Electrical double layer of the charged particles (eq. (3) and (4)) to produce strong oxidizing hydroxyl radicals which can promote the oxidation of organic compounds (Eqs. (5) and (6)).

4.2. Photocatalytic activity

In order to achieve effective degradation, factors influencing reaction such as catalyst concentration and reactant concentration were optimized. The catalyst amount of 0.025, 0.05 and 0.075 were tested and the reactant concentration was varied with 5, 10 and 15 ppm of methylene blue. Catalyst concentration of 0.05g/L and reactant concentration of 10 ppm were chosen as the optimized condition for the photocatalytic activity. The concentration remained after attaining adsorption-desorption equilibrium was taken as the initial concentration for plotting the results.

4.3. Effect of different catalysts

The linear transform of kinetic plot showed that the reaction followed the pseudo first order kinetics. From the kinetic plot (Fig 7a, 7b) , it is found that the increase in reaction time increased the activity of all the catalysts except GO. The activity of different catalysts follows the trend: nano- TiO_2>C - TiO_2> WO_3> GO. photocatalytic degradation of dichlorvos was carried out using pure GO and results showed that it does not influence on the activity. However, it showed higher adsorption than the other catalysts.

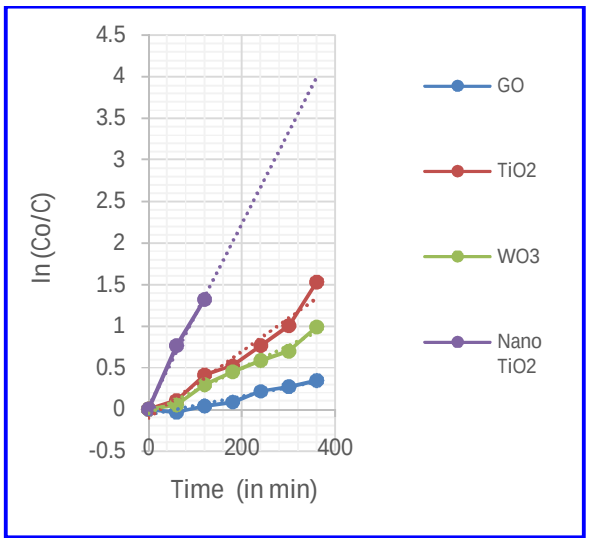

Fig. 7a: Kinetics plot of dichlorvos on different catalysts without oxygen purging

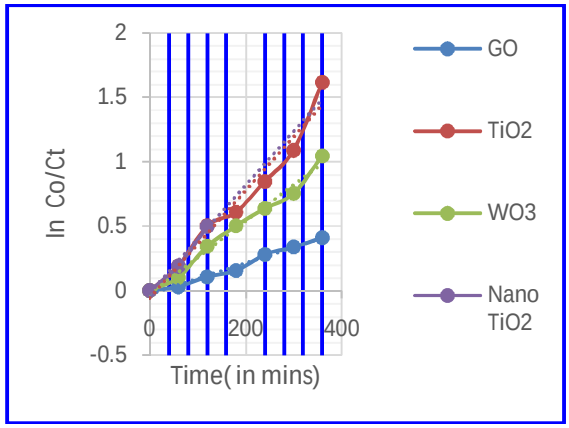

Fig. 7b: Kinetics plot of dichlorvos on different catalysts

Fig.8 showsthe degradation profile represented in percentage(%) of degradation. Among the other catalysts, nano-TiO_2 showed the fastest as well as complete degradation. The next highly active catalyst is C - TiO_2. However, on comparing $WO_3$with C - TiO_2, latter is the highly active one. Since C - TiO_2 and WO_3 have lower surface area, they failed to show significant increase in adsorption as well as photocatalytic degradation. Photocatalytic activity mainly depends on effective charge carrier separation.

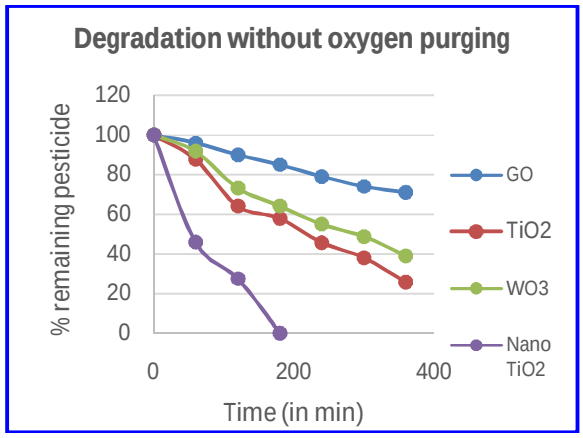

Fig. 8 : Degradation of dichlorvos on different catalysts

4.4 Influence of external oxygen

To study the influence of external oxygen, the air was purged during the reaction. This additional purging of air improves the well dispersion of catalyst particles**.** Fig 9 shows the results of influence of external oxygen. The role of external oxygen in photocatalysis is expected to occur via production of super oxide ion during the reaction as given in reaction 7 and 8.

$$\text{Semi-conductor} + h\nu \rightarrow e^- + h^+ \qquad (7)$$

$$e^- + O_2 \rightarrow O_2^- \text{ (super oxide ion)} \quad (8)$$

This super oxide ion can further oxidizes the reactant molecules. Hence, the oxidation expected to be taken place in two ways: (i) by valence band hole oxidation of water and (ii) conduction band reduction of oxygen. GO has higher conduction band which can firmly reduce the oxygen as given in reaction 8. Hence, the oxidation of dichlorvos taken place via both oxidation by hole as well as by superoxide ion. This improved the photocatalytic activity of nano TiO_2, C-TiO_2 and WO_3.

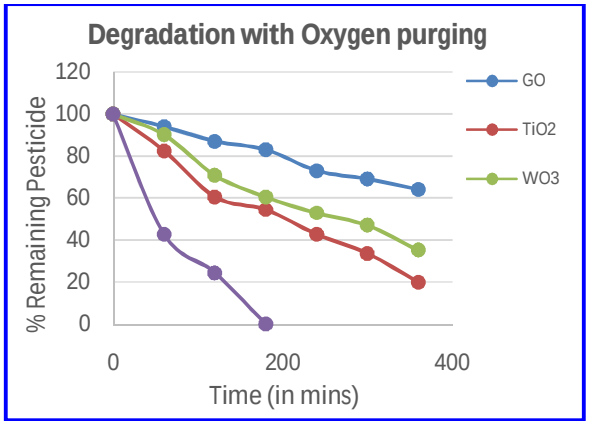

Fig. 9: Influence of external oxygen

5. CONCLUSIONS

Materials synthesized were characterized by different physico-chemical techniques. These materials then tested for the photocatalytic degradation of Dichlovos. Characterization results showed that more number of TiO_2 particles are present over the surface and WO_3showed larger and irregular shaped particles seen on the surface. These were confirmed with FTIR, and SEM analysis. Hence, nano - TiO_2 showed higher activity than C- TiO_2, and WO_3.

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